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64 **Fluorinated vinyl ethers, copolymers thereof, and precursors thereof.**

67 Vinyl ethers and acyl fluorides of the formula  
(CF<sub>2</sub>CFOR)<sub>n</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>OR where n is 0 or 1 and R is CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>. The vinyl



ethers can be copolymerized with, e.g., tetrafluoroethylene, to provide copolymers which are useful as electrical insulation and as the sheath portion of optical fibers, and can be converted to known ion exchange polymers having carboxylic groups which are useful, e.g. in the form of permionic membrane, for separating the compartments of a chloralkali cell.

**EP 0 150 618 A2**

TITLE

FLUORINATED VINYL ETHERS, COPOLYMERS  
THEREOF, AND PRECURSORS THERETO

BACKGROUND OF THE INVENTION

5 Fluorinated vinyl monomers have proved to be  
useful intermediates for making highly fluorinated  
and perfluorinated polymers and copolymers which are  
useful, e.g., as electrical insulation, permselective  
membranes, and the sheath (cladding) layer of optical  
10 fibers.

It is an object of this invention to provide  
novel fluorinated vinyl ether monomers, precursors  
thereto, and methods for making same.

15 It is another object of this invention to  
provide novel highly fluorinated copolymers  
containing ether linkages.

It is yet another object to provide new and  
improved methods for making certain known fluorinated  
vinyl ethers which contain carboxylate functional  
20 groups.

It is yet a further object to provide a  
novel method for making known highly fluorinated and  
perfluorinated ion exchange polymers which contain  
carboxylate functional groups.

SUMMARY OF THE INVENTION

25 According to the present invention, there  
are provided a chemical compound having the  
structural formula

30 
$$\text{CF}_2=\text{CFO}(\text{CF}_2\text{CFO})_n\text{CF}_2\text{CF}_2\text{CF}_2\text{OR}$$
 wherein n is 0 or  
CF<sub>3</sub>

1 and R is CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>, copolymers thereof, and  
precursors thereto.

35 There are also provided, according to the  
present invention, improved processes for preparing

certain fluorinated vinyl ether monomers which contain carboxylate functional groups.

There is further provided, according to the present invention, a new method for making some fluorinated ion-exchange polymers which contain carboxylate functional groups.

#### DETAILED DESCRIPTION OF THE INVENTION

The vinyl monomers of the invention can be prepared by a series of steps starting with the known methyl 3-methoxytetrafluoropropionate (see, e.g., U.S.P. 2,988,537), 3-methoxytetrafluoropropionic acid, or 3-methoxytetrafluoropropionyl fluoride (see, e.g., U.S.P. 3,113,967). If the free carboxylic acid is used as the starting point, it is first transformed to the acyl fluoride; this can be done, e.g., (1) in two steps by (a) reacting the free acid with any of a variety of reagents such as  $\text{PCl}_5$ ,  $\text{POCl}_3$ ,  $\text{SOCl}_2$  or benzoyl chloride at almost any pressure at a temperature of  $25^\circ$  to  $250^\circ\text{C}$  to make 3-methoxytetrafluoropropionyl chloride and (b) reacting the latter with any of a variety of reagents such as alkali metal fluorides or  $\text{SbF}_3$  with or without a solvent at almost any pressure at a temperature of  $50^\circ$  to  $400^\circ\text{C}$ , or (2) in one step by reacting the acid with  $\text{SF}_4$  at room temperature and autogenous pressure. If the ester is used as the starting point, it is first hydrolyzed to the free carboxylic acid, for example by hydrolysis with acid or base. The acyl fluoride is also directly available by reaction of methyl trifluorovinyl ether and carbonyl fluoride (see J. Amer. Chem. Soc. 84, 4275 (1962)).

The immediate precursors of the vinyl monomers of the invention are prepared by reacting 3-methoxytetrafluoropropionyl fluoride with

hexafluoropropylene oxide (HFPO). The reaction is carried out in the presence of fluoride ion catalyst and a reaction medium.

5 The fluoride ion catalyst is provided by a fluoride compound which dissolves in the reaction medium to the extent of at least 0.001% by weight at 20°C. Suitable fluoride compounds are potassium, rubidium and cesium fluorides. A preferred fluoride compound is potassium fluoride, as its use results in  
10 higher yields of the desired product. The fluoride compound can be used in amounts of about 0.01 to 10 equivalents, preferably about 0.05 to 0.5 equivalent, per mole of 3-methoxytetrafluoropropionyl fluoride employed.

15 The reaction medium can be an aprotic liquid in which the fluoride catalyst is soluble to the extent of at least 0.001% by wt. at 20°C (component A). Suitable examples include the so-called glymes (mono-, di-, tri- and tetraethyleneglycol dimethyl  
20 ether); lactones such as 4-butyrolactone, 5-valerolactone and 6-caprolactone, and mononitriles such as acetonitrile and propionitrile. Triglyme and tetraglyme are preferred because they are more easily separated from the product.

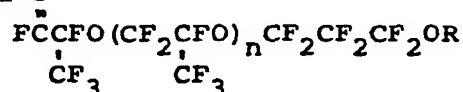
25 The reaction medium can also be, and preferably is, a mixture of 2 to 50% by volume of component A and 98 to 50% by volume of a second aprotic liquid (component B). Suitable examples of component B include dinitriles such as malono-,  
30 succino-, glutaro-, adipo-, methylmalono-, pimelo-, subero-, and phthalo-nitrile; and tetramethylenesulfone. The dinitriles are preferred, and adiponitrile is especially preferred. More preferably, component A constitutes 85 to 98% by  
35 volume of the medium, and component B is 15 to 2% by

volume. Most preferably, component A constitutes 85 to 95% by volume of the medium, and component B is 5 to 15% by volume.

The reaction of

- 5 3-methoxytetrafluoropropionyl fluoride with HFPO is exothermic. Reaction temperatures can range from about 0° to 100°C, with temperatures between 25° and 70°C being preferred. Pressure is not critical, and subatmospheric and superatmospheric pressures are  
10 operable; pressures close to atmospheric are preferred. The pressure in the reaction vessel can be controlled by regulating the rate of supply of gaseous HFPO.

- The precursor compounds so made have the  
15 structural formula O



- where R is CH<sub>3</sub>. When 3-methoxytetrafluoropropionyl  
20 fluoride reacts with 1 equivalent of HFPO, the precursor compound so made has the indicated structure where n is 0. That precursor compound can in turn react with a second equivalent of HFPO to make the precursor compound where n=1. Small amounts of products wherein more units of HFPO are  
25 incorporated are usually also formed. The relative amounts of the precursor compounds where n=0 and n=1 so made can be controlled by controlling the number of equivalents of HFPO used as reactant; relatively lesser amounts of HFPO favor formation of the  
30 precursor compound where n=0, and relatively larger amounts of HFPO favor formation of the precursor compound where n=1. If the precursor compounds are made by reacting HFPO with  
35 3-ethoxytetrafluoropropionyl fluoride, the precursor compounds have the indicated structural formula where R is C<sub>2</sub>H<sub>5</sub>.

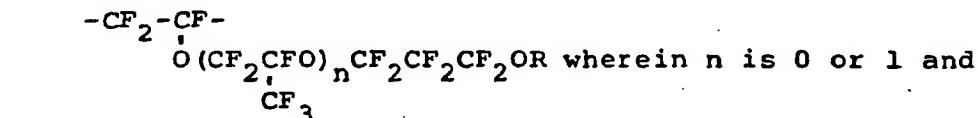
Such precursor compound is then subjected to a dehalocarbonylation reaction, wherein the elements of  $\text{COF}_2$  are removed to produce the novel vinyl monomers  $\text{CF}_2 = \text{CFO}(\text{CF}_2\text{CFO})_n\text{CF}_2\text{CF}_2\text{CF}_2\text{OR}$

5



where  $n$  is 0 or 1 and  $R$  is  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ . This reaction is suitably carried out by contacting the precursor compound with at least one member of the group consisting of  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_2\text{CO}_3$  at a temperature of at least  $170^\circ\text{C}$ , preferably  $190$  to  $260^\circ\text{C}$ .

These vinyl ether monomers can be copolymerized with other fluorinated monomers to make novel copolymers. Suitable comonomers include  $\text{CX}_2 = \text{CX}_2$  where the four  $X$ 's are four fluorines or three fluorines and one chlorine. Such copolymers comprise about 70 to 95 mol %  $-\text{CX}_2-\text{CX}_2-$  units where the four  $X$ 's are as defined above, and about 5 to 30 mol % of substituted ethylene units of the formula



$R$  is  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ , the substituted ethylene units being randomly positioned throughout the copolymer chain. The copolymers wherein the four  $X$ 's are four fluorines are preferred. These copolymers are useful, e.g., as insulation on electrical conductors, base for printed circuits, and as the sheath (cladding) portion of optical fibers.

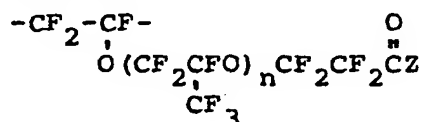
The copolymers can be prepared by general polymerization techniques developed for homo- and copolymerizations of fluorinated ethylenes, particularly those employed for tetrafluoroethylene

which are described in the literature. Nonaqueous techniques for preparing the copolymers include that of U.S. Patent No. 3,041,317, that is, by the polymerization of a mixture of the major monomer therein, such as tetrafluoroethylene, and the fluorinated vinyl ether monomer in the presence of a free radical initiator, preferably a peroxydicarbonate, a perfluorocarbon peroxide or azo compound, at a temperature in the range 0-200°C and at pressures in the range of  $10^5$  to  $2 \times 10^7$  pascals (1-200 Atm.) or higher. The nonaqueous polymerization may, if desired, be carried out in the presence of a fluorinated solvent. Suitable fluorinated solvents are inert, liquid, perfluorinated hydrocarbons, such as perfluoromethylcyclohexane, perfluorodimethylcyclobutane, perfluorooctane, perfluorobenzene and the like, and inert, liquid chlorofluorocarbons such as 1,1,2-trichloro-1,2,2-trifluoroethane, and the like.

Aqueous techniques can also be used for preparing the copolymer, and include contacting the monomers with an aqueous medium containing a free-radical initiator to obtain a slurry of polymer particles in non-water-wet or granular form, as disclosed in U.S. Patent No. 2,393,967, or contacting the monomers with an aqueous medium containing both a free-radical initiator and a telogenically inactive dispersing agent, to obtain an aqueous colloidal dispersion of polymer particles, and coagulating the dispersion, as disclosed, for example, in U.S. Patent No. 2,559,752 and U.S. Patent No. 2,593,583.

The above copolymers can, if desired, be converted to esters of known fluorinated ion-exchange polymers by treatment with a strong acid at a

temperature of at least 50°C but below the decomposition temperature of the above-described copolymers, the product ion-exchange polymers, and the strong acid. The strong acids which are suitable for treatment of the above copolymers to make fluorinated ion-exchange copolymers or precursors thereto are suitably, e.g.,  $\text{H}_2\text{SO}_4$ ,  $\text{ClSO}_3\text{H}$ ,  $\text{FSO}_3\text{H}$  or  $\text{R}_f\text{SO}_3\text{H}$  where  $\text{R}_f$  is a perfluorinated  $\text{C}_1$  to  $\text{C}_8$  group, or Lewis acids in which the halide is fluoride such as  $\text{SbF}_5$ . Temperatures of 80 to 150°C are preferred. Such treatment of the above copolymers gives copolymers comprising about 70 to 95 mol %  $-\text{CX}_2-\text{CX}_2-$  units wherein the four X's are four fluorines or three fluorines and one chlorine, and about 5 to 30 mol % of substituted ethylene units of the formula



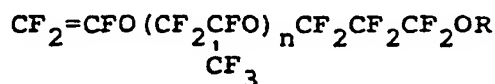
where n is 0 or 1, Z is F or  $\text{OR}'$ , and  $\text{R}'$  is at least one member of the group consisting of R and H, the substituted ethylene units being randomly positioned throughout the copolymer chain. The carboxylic ester polymers can be hydrolyzed to known carboxylic acid polymers which are useful for ion-exchange purposes. Some hydrolysis of the ester polymers may occur to varying degree during the treatment of the ether-containing polymers with strong acid, the amount of hydrolysis varying with the acid and conditions used.

Such fluorinated polymers which contain carboxylic acid functional groups can be employed in various known ion-exchange uses. One such use is in the form of a permselective membrane for separating



the anode and cathode compartments of a chloralkali electrolysis cell; the ion-exchange capacity of the polymer for such use should be in the range of 0.7 to 1.5 meq/g (milliequivalents/gram), preferably 0.8 to 1.3 meq/g.

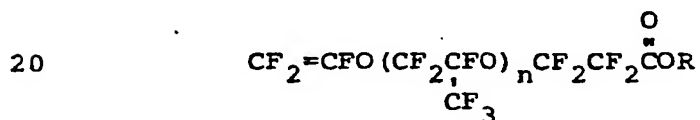
The vinyl ether monomers



or their bromine adducts  $\text{CF}_2\text{BrCFBrO}(\text{CF}_2\underset{\text{CF}_3}{\underset{|}{\text{CFO}}})_n\text{CF}_2\text{CF}_2\text{CF}_2\text{OR}$

i.e., compounds of the formula  $\text{YO}(\text{CF}_2\underset{\text{CF}_3}{\underset{|}{\text{CFO}}})_n\text{CF}_2\text{CF}_2\text{CF}_2\text{OR}$

wherein Y is  $\text{CF}_2=\text{CF}-$  or  $\text{CF}_2\text{BrCFBr}-$ , can also be converted respectively to vinyl ether monomers which contain carboxylic ester functional groups, having the structural formula



or their bromine adducts  $\text{CF}_2\text{BrCFBrO}(\text{CF}_2\underset{\text{CF}_3}{\underset{|}{\text{CFO}}})_n\text{CF}_2\text{CF}_2\overset{\text{O}}{\overset{||}{\text{COR}}}$ ,

i.e., compounds of the formula  $\text{YO}(\text{CF}_2\underset{\text{CF}_3}{\underset{|}{\text{CFO}}})_n\text{CF}_2\text{CF}_2\overset{\text{O}}{\overset{||}{\text{COR}}}$

wherein Y is  $\text{CF}_2=\text{CF}-$  or  $\text{CF}_2\text{BrCFBr}-$ , n is 0 or 1, and R is  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ . When Y is  $\text{CF}_2=\text{CF}-$ , this conversion is suitably carried out by treatment with a strong acid at a temperature of at least  $25^\circ\text{C}$ , but below the decomposition temperatures of both the starting vinyl ether monomer and the product vinyl

carboxylic ester monomer and the strong acid, preferably at 70 to 100°C; above about 100°C, some decomposition of the vinyl ether compound may occur. When Y is  $\text{CF}_2\text{BrCFBr-}$ , the conversion is suitably carried out by treatment with a strong acid at a temperature of at least 25°C, but below the decomposition temperatures of both the starting brominated ether compound and the product brominated carboxylic ester compound and the strong acid, preferably at 100 to 150°C. The strong acids which are suitable for treatment of the vinyl ether monomers or their bromine adducts to make compounds containing carboxylic ester functional groups are suitably, e.g.,  $\text{H}_2\text{SO}_4$ ,  $\text{ClSO}_3\text{H}$ ,  $\text{FSO}_3\text{H}$  or  $\text{R}_f\text{SO}_3\text{H}$  where  $\text{R}_f$  is a perfluorinated  $\text{C}_1$  to  $\text{C}_8$  group. The resulting vinyl monomers containing carboxylic ester groups can be copolymerized with other fluorinated ethylenically unsaturated monomers, such as  $\text{CX}_2=\text{CX}_2$  where X is as defined hereinabove, to provide copolymers which can be hydrolyzed to the known fluorinated carboxylic acid ion exchange polymers referred to above.

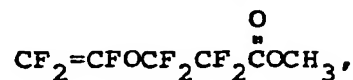
The bromine adducts are suitably made by reaction of bromine with the vinyl ether monomers. Addition of bromine to the olefinic bond is facilitated by irradiation with ultraviolet and/or visible light, as from a commercially available sun lamp. An inert solvent can be used but is not necessary.

The bromine adduct of the vinyl ether monomer which contains a carboxylic ester functional group can suitably be debrominated to the vinyl ether monomer which contains a carboxylic ester functional group by, e.g., treatment with zinc.

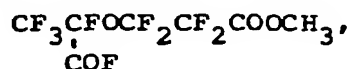
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Preparation of the vinyl ether monomer which contains a carboxylic ester functional group via the three step route of brominating the vinyl ether monomer, acid treatment to convert the -CF<sub>2</sub>OR moiety to the -COOR group, and debromination, is particularly advantageous because the brominated compound is more thermally stable than the vinyl ether compound.

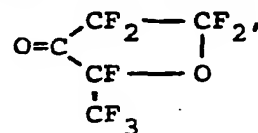
Although that vinyl monomer with carboxylic ester group, referred to in the previous paragraph, where n is 0 and R is CH<sub>3</sub>, i.e.,



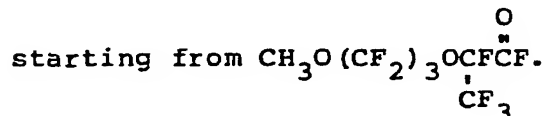
is a known compound, the method disclosed herein for making it according to the present invention is superior to a known method, the dehalocarbonylation of



due to a sequence of reactions in the known method starting with cyclization to form



which known method yields but little of the desired vinyl carboxylic ester monomer. It is also superior to another known method which starts with epoxidation of 1,1,2,3,3-pentafluoro-3-chloropropene-1. The method disclosed herein, ending with treatment of the vinyl ether monomer with strong acid, provides an overall yield of about 50% for the four steps



To further illustrate the innovative aspects of the present invention, the following examples are provided.

EXAMPLES

All temperatures specified herein are in °C.

Example 1

A. Preparation of  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{COOH}$   
(3-Methoxytetrafluoropropionic Acid)

5 A mixture of 32 g sodium hydroxide, 400 g water and 152 g methyl 3-methoxytetrafluoropropionate was stirred at room temperature until a single liquid layer was obtained. The product was acidified with  
10 37% aqueous HCl and the lower layer separated. The aqueous layer was extracted four times with 50 ml ethyl ether and the combined ether extracts and lower layer distilled to give 103.3 g (73.4%)  
15 3-methoxytetrafluoropropionic acid, b.p. 85-86° at 20 mm.

B. Preparation of  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{COCl}$   
(3-Methoxytetrafluoropropionyl Chloride)

A mixture of 47.4 g  
3-methoxytetrafluoropropionic acid and 67.3 g  
20 phosphorous pentachloride was heated and the contents distilled to obtain a pale yellow liquid boiling to 102°. Redistillation of this liquid yielded 49.8 g (95.2%) 3-methoxytetrafluoropropionyl chloride, b.p. 84-86°.

C. Preparation of  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{COF}$   
(3-Methoxytetrafluoropropionyl Fluoride)

A mixture of 34.8 g potassium fluoride, 100 ml tetramethylene sulfone and 49.8 g  
3-methoxytetrafluoropropionyl chloride was slowly  
30 heated to give 35.4 g of colorless liquid (77.8%) whose infrared spectrum was identical to 3-methoxytetrafluoropropionyl fluoride.

D. Preparation of  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{O}(\overset{\text{CF}_3}{\underset{|}{\text{C}}}\text{FCF}_2\text{O})_n\overset{\text{CF}_3}{\underset{|}{\text{C}}}\text{FCOF}$

35 where n = 0 and 1.

(2-(3-Methoxyhexafluoropropoxy)tetrafluoropropionyl fluoride and

2-[2-(3-Methoxyhexafluoropropoxy)hexafluoropropoxy]-tetrafluoropropionyl fluoride)

- 5 A mixture of 1.5 g potassium fluoride, 56 g of a 9/1 volume/volume mixture of adiponitrile and tetraglyme and 44.3 g of 3-methoxytetrafluoropropionyl fluoride were reacted at 30° with 44 g of hexafluoropropylene oxide. The lower layer of the reaction mixture was separated and distilled to give 28.6 g (49%) of the product where  $n=0$ , b.p. 50° at 100 mm, and 23.0 g (26%) of the product where  $n=1$ , b.p. 90° at 100 mm.

Example 2

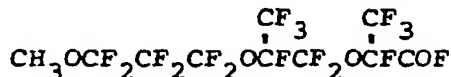
- 15 Preparation of  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$  (3-Methoxyhexafluoropropyltrifluoroethenyl ether)

- A glass tube (2.5 cm diameter) packed with 125 g of dry trisodium phosphate was heated to 225° and 30.4 g 2-(3-methoxyhexafluoropropoxy)-tetrafluoropropionyl fluoride was passed through it at a rate of 0.48 ml per minute. The crude product was distilled to give 17.0 g 3-methoxyhexafluoropropyltrifluoroethenyl ether, b.p. 54° at 200 mm, whose structure was consistent with its infrared spectrum and  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra.

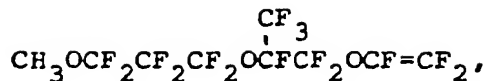
Example 3

- 30 Preparation of  $\text{CH}_3\text{OCF}_2\text{CF}_2\overset{\text{CF}_3}{\underset{|}{\text{CF}_2}}\text{OCF}\overset{\text{CF}_3}{\underset{|}{\text{CF}_2}}\text{OCF}=\text{CF}_2$

- A tube containing 125 g of dry trisodium phosphate was heated to 225° and 19.8 g

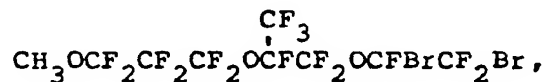


- 35 added at a rate of 0.48 ml per minute. The crude product was distilled to give 10.8 g



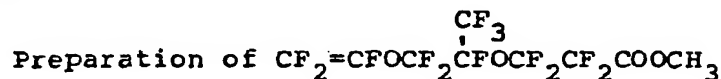
b.p. 80-82° at 100 mm, whose structure was consistent  
5 with its infrared and  $^{19}\text{F}$  NMR spectra.

For purposes of further confirming the  
- structure of the product, a small portion of the  
above vinyl ether was reacted with excess bromine  
under irradiation of a "GE Sun Lamp." The crude  
10 product was washed with aqueous sodium bisulfite and  
distilled to give



b.p. 196°, whose structure was consistent with its  
15 infrared and  $^{19}\text{F}$  NMR spectra.

Example 4



20 A mixture of 10.0 g

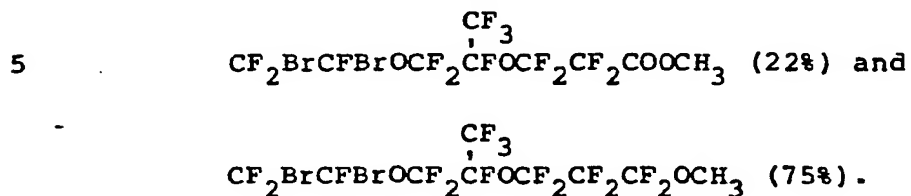


and 10.8 g 96% sulfuric acid was stirred at room  
25 temperature for 16 hours. The mixture was added to  
100 ml water, and 9.3 g of a lower layer, almost all  
starting material, was recovered. The 9.3 g  
recovered material was heated at 80° for 16 hours  
with 15 ml 96% sulfuric acid and the mixture added to  
30 50 ml water to give 7.8 g product. Gas  
chromatographic analysis showed the product to  
contain 74% starting material and 21%



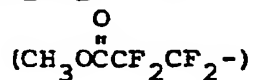
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For purposes of confirming the structure of the product, a portion of the product was brominated to give material containing

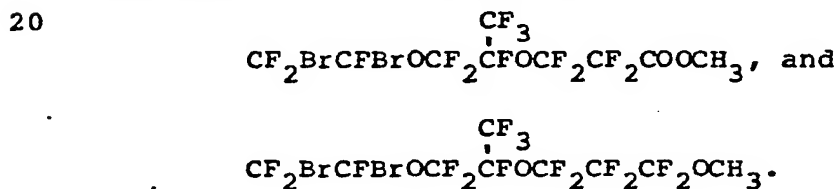


10 The gas chromatographic retention times of these products were identical to those of authentic samples. The IR spectrum of the mixture showed an absorption at 5.6 microns ( $\text{COOCH}_3$ ). The  $^1\text{H}$  NMR showed two singlets at 3.52 ppm

15 ( $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_2-$ ) and 3.74 ppm



in the ratio of 1/3.36 while the  $^{19}\text{F}$  NMR was consistent with a mixture of



25 The remainder of the reaction product was heated at  $100^\circ$  for 4 hours and then added to 50 ml water to give 4.5 g of product which contained 51% starting material and 38% product. An infrared spectrum of the material corresponding to the 38%

30 product peak was identical to that of an authentic sample of



35

Example 5A. Preparation of  $\text{CF}_2\text{BrCFBrOCF}_2\text{CF}_2\text{CF}_2\text{OCH}_3$ .

5 A 4.7 g mixture of  $\text{CF}_2=\text{CFO}(\text{CF}_2)_3\text{OCH}_3$   
(ca. 70 mol %) and  $\text{CClF}_2\text{CCl}_2\text{F}$  (ca. 30 mol %) was  
reacted with excess bromine under irradiation of a GE  
Sun Lamp. The excess bromine was destroyed with  
aqueous sodium bisulfite, and the product (lower  
layer, 4.2g) was identified by gas chromatographic  
and NMR analyses to be  $\text{CF}_2\text{BrCFBrOCF}_2\text{CF}_2\text{CF}_2\text{OCH}_3$   
10 containing a trace of  $\text{CClF}_2\text{CCl}_2\text{F}$ .

B. Preparation of  $\text{CF}_2\text{BrCFBrOCF}_2\text{CF}_2\text{COOCH}_3$ .

A mixture of 4.2 g  
 $\text{CF}_2\text{BrCFBrOCF}_2\text{CF}_2\text{CF}_2\text{OCH}_3$  and 25 ml 96%  
15 sulfuric acid was heated at  $120^\circ$  for 4 hours and  
stirred at room temperature for 16 hours. The  
reaction mixture was added to 200 ml cold water and  
the lower layer separated. The aqueous layer was  
extracted with  $\text{CClF}_2\text{CCl}_2\text{F}$ , and gas  
20 chromatographic and NMR analysis showed the presence  
of  $\text{CF}_2\text{BrCFBrOCF}_2\text{CF}_2\text{COOCH}_3$  and  $\text{CClF}_2\text{CCl}_2\text{F}$   
as the only halogenated compounds.

C. Preparation of  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{COOCH}_3$ .

When 29.2g  $\text{CF}_2\text{BrCFBrOCF}_2\text{CF}_2\text{COOCH}_3$  in  
25 5ml tetraglyme was added to 6.5g zinc dust, 0.1g  
iodine and 40 ml tetraglyme, an exothermic reaction  
was observed. The reaction mixture was distilled at  
100 mm Hg pressure to give 15.1g (84% yield)  
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{COOCH}_3$  whose structure was  
30 confirmed by comparison of its infrared spectrum and  
gas chromatographic retention time with those of an  
authentic sample.

Example 6

35 Copolymerization of  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$  and  
Tetrafluoroethylene.



A mixture of 17.0 g  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ ,

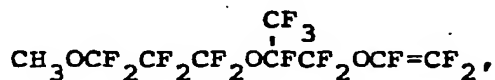
35.0 g 1,1,2-trifluoro-1,2,2-trichloroethane (F113),  
0.02 g bis (4-t-butylcyclohexyl)peroxydicarbonate and  
20 g tetrafluoroethylene was heated at 45° for one  
hour and 50° for three hours to give a polymeric  
gel. The polymer, 6.5 g, was isolated by washing  
three times with methanol and drying. The infrared  
spectrum of a thin film pressed at 300° was  
consistent with a copolymer of tetrafluoroethylene and  
 $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ . The  $^{19}\text{F}$  NMR spectrum of the  
copolymer was also consistent with this structure and  
showed that the molar ratio of  $\text{CF}_2=\text{CF}_2$  to

$\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$  was 5.06 to 1.00.

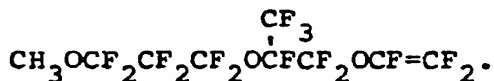
#### Example 7

Copolymerization of  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_2\overset{\text{CF}_3}{\underset{|}{\text{OCF}}}\text{CF}_2\text{OCF}=\text{CF}_2$   
and Tetrafluoroethylene.

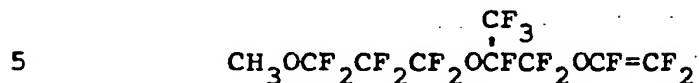
A mixture of 10.7 g



20 g 1,1,2-trifluoro-1,2,2-trichloroethane (F113),  
0.02 g bis (4-t-butylcyclohexyl)peroxydicarbonate and  
15 g tetrafluoroethylene was heated at 45° for one  
hour and 50° for three hours to give a colorless  
gel. A white polymer, 1.8 g, was isolated by washing  
three times with methanol and drying. The infrared  
spectrum of a thin film pressed at 275° was  
consistent with a copolymer of tetrafluoroethylene and



The  $^{19}\text{F}$  NMR spectrum was also consistent with this structure and showed the molar ratio of tetrafluoroethylene to



to be 6.50 to 1.00.

Example 8

Hydrolysis of  $\text{CF}_2=\text{CF}_2/\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCH}_3$

10 Copolymer and Use of Hydrolyzed Copolymer in a Chloralkali Cell.

A mixture of 25 ml chlorosulfonic acid and 2.3 g of a copolymer of  $\text{CF}_2=\text{CF}_2$  and  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCH}_3$  was stirred and heated for 5  
15 hours at  $100^\circ$ . The reaction mixture was carefully added to 500 ml ice and ice water and the polymer recovered by filtration. The polymer was heated in 30 ml refluxing anhydrous methanol for 16 hours,  
20 filtered and dried. A thin film of the product could be pressed at  $300^\circ$  whose infrared spectrum was identical to that of a film of copolymer prepared by the copolymerization of  $\text{CF}_2=\text{CF}_2$  and  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{COOCH}_3$ .

25 A larger film of the material was pressed at  $310^\circ$ . It was hydrolyzed in a mixture of 300 ml water, 375 g methanol and 75 ml 10N sodium hydroxide at  $60^\circ$  for 66 hrs to give a film of the corresponding sodium salt 7.6 mils in thickness. The film was  
30 mounted in a chloralkali cell and produced 31.3% NaOH with a current efficiency of 94.2% at 4.34 volts.

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CLAIMS

1. A vinyl ether having the structural formula  

$$\text{CF}_2=\text{CFO}(\text{CF}_2\overset{\text{CF}_3}{\underset{|}{\text{CFO}}})_n\text{CF}_2\text{CF}_2\text{CF}_2\text{OR}$$
 wherein n is 0 or 1 and R is  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ .
2. A vinyl ether according to claim 1 wherein n is 0 and R is  $\text{CH}_3$ .
3. A vinyl ether according to claim 1 wherein n is 1 and R is  $\text{CH}_3$ .
4. A copolymer comprising 70 to 95 mol %  $-\text{CX}_2-\text{CX}_2-$  units wherein the four X's are four fluorines or three fluorines and one chlorine, and 30 to 5 mol % of substituted ethylene units derived from a vinyl ether as claimed in claim 1, 2 or 3, said substituted ethylene units being randomly positioned throughout the copolymer chain.
5. A copolymer according to claim 4 wherein the four X's are four fluorines, n is 0 and R is  $\text{CH}_3$ .
6. A copolymer according to claim 4 wherein the four X's are four fluorines, n is 1 and R is  $\text{CH}_3$ .
7. An acyl fluoride having the structural formula  

$$\overset{\text{O}}{\underset{|}{\text{FCCFO}}}(\text{CF}_2\overset{\text{CF}_3}{\underset{|}{\text{CFO}}})_n\text{CF}_2\text{CF}_2\text{CF}_2\text{OR}$$
 wherein n is 0 or 1 and R is  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ .
8. An acyl fluoride according to claim 7 wherein n is 0 and R is  $\text{CH}_3$ .
9. An acyl fluoride according to claim 7 wherein n is 1 and R is  $\text{CH}_3$ .

